DEVELOPMENT OF AN IMPLEMENTATION PLAN FOR ATMOSPHERIC CARBON MONITORING IN CALIFORNIA

PIER FINAL PROJECT REPORT

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Preface

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace. The PIER Program, managed by the California Energy Commission (Energy Commission), annually awards up to $62 million to conduct the most promising public interest energy research by partnering with Research, Development, and Demonstration (RD&D) organizations, including individuals, businesses, utilities, and public or private research institutions.

PIER funding efforts are focused on the following RD&D program areas:

- Buildings End-Use Energy Efficiency
- Energy-Related Environmental Research
- Energy Systems Integration
- Environmentally Preferred Advanced Generation
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies

What follows is the final report for the PIER-EA Exploratory Grant contract, contract number 500-02-004, work authorization number MR-015, conducted by the E. O. Lawrence Berkeley National Laboratory. The report is entitled *Development of an Implementation Plan for Atmospheric Carbon Monitoring in California.* This project contributes to the Energy-Related Environmental Research program.

For more information on the PIER Program, please visit the Energy Commission's website www.energy.ca.gov/pier/ or contract the Energy Commission at (916) 654-4628.

Table of Contents

List of Figures

List of Tables

Abstract

This report describes the design of atmospheric CO_2 concentration measurements that, in combination with other measurements and models, would be used to quantify regionally distributed CO_2 exchanges from California's terrestrial ecosystems and CO_2 emissions from fossil fuel combustion. Using models of net ecosystem CO_2 exchange (NEE), fossil fuel CO_2 emissions, and regional meteorology, the LBNL research team predicted CO_2 concentration "signals" in the atmosphere. Researchers subdivided the CO_2 sources into four components: (1) NEE inside California, (2) NEE outside California, (3) fossil fuel CO_2 inside California, and (4) fossil fuel CO_2 outside California. Maps of predicted atmospheric CO_2 concentration signals from these four sources largely mirror the instantaneous emissions near strong sources, but plumes of CO_2 enriched or depleted air are predicted to advect far from their sources. Using the predicted concentration signals, LBNL identified a baseline set of observing stations from existing and possible future sites that could be used to characterize in-state and out-of-state ecosystem and fossil fuel contributions to atmospheric CO_2 concentrations. The research team also identified a measurement protocol for making concentration measurements at the stations. Although beyond the scope of this project, future work should estimate the uncertainties in estimating California's NEE that would be obtained using atmospheric concentration data from the stations identified herein.

Keywords: greenhouse gas emissions, atmospheric monitoring, inverse methods, land-surface CO_2 modeling

Executive Summary

Introduction

Carbon dioxide (CO_2) is a greenhouse gas (GHG) that is emitted as the result of combusting fossil fuels for electricity production, transportation, industry, and other uses. Worldwide, roughly half of the CO_2 emitted by fossil fuel combustion remains in the atmosphere, leading to sustained increases in atmospheric CO_2 concentrations. In-state electricity generation accounts for about 16% of California's anthropogenic CO_2 emissions.[1] Because these emissions contribute to human-induced climate change, the California Energy Commission (Energy Commission) has identified the study of CO_2 and other GHGs as a priority area for research. Future cost and production strategies for electricity generation may be affected by economic and policy responses to global warming. Therefore, it will be important to determine the contribution of fossil fuel combustion and other sources of CO_2 exchange to atmospheric CO_2 levels. Currently, the Energy Commission estimates CO_2 emissions using accounting data for fossil fuel emissions and a combination of inventory surveys and simple models for net ecosystem exchange (NEE)[2] of CO_2. The net ecosystem fluxes occur continuously and uncertainties associated with these fluxes are poorly quantified.

At the national level, the carbon cycle community was posed with the analogous problem of providing defensible estimates of net CO_2 (and other GHG) exchange. In response, the research community suggested a North American Carbon Program (NACP) to provide a robust approach for reducing the uncertainties in regional CO_2 exchange estimates. The NACP is envisioned to combine inventory methods of biosphere carbon stocks and fossil fuel emissions, direct CO_2 flux measurements,[3] and measurements of atmospheric CO_2 concentrations, all coupled within an inverse analysis[4] employing ecosystem-atmosphere models of NEE and atmospheric transport.

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[1] California Energy Commission. November 2001. *Inventory of California Greenhouse Gas Emissions and Sinks: 1990–1999.* P600-02-001F. Figure ES-8.

[2] *NEE* is the net flow of CO_2 from terrestrial ecosystems to the atmosphere. For both NEE and fossil fuel CO_2 emissions, fluxes are defined so that a positive flux causes an increase in atmospheric CO_2 concentrations.

[3] Direct flux measurements quantify CO_2 exchange over a limited area using micrometeorological methods. For example, the eddy covariance method employs rapid measurements of vertical wind velocity and CO_2 concentration to calculate the net flux of CO_2 as average of CO_2 concentration weighted by vertical velocity. Equivalently, the flux can be viewed as the net difference in the amount of CO_2 carried upward minus downward with the atmospheric eddies.

[4] Mathematical inverse methods estimate the spatial and temporal distribution of surface fluxes that are most consistent with measurements of CO_2 concentration by working backward from concentration to flux under the assumption that CO_2 concentrations are the result of surface fluxes being transported in the atmosphere by meteorology. See for example, Kasibhatla, P., and American Geophysical Union. 2000. *Inverse methods in global biogeochemical cycles.* Washington, D.C.: American Geophysical Union.

Measurement of CO_2 concentration gradients on regional scales is challenging because the concentration differences generated by NEE are in the range of < 1 part per million (ppm) to approximately 20 ppm. Sufficiently accurate measurements can be made for signals greater than about 1 ppm from the instrument perspective, because the state-of-the-art in measurement accuracy is approximately 0.2 ppm of CO_2. A careful examination of the expected concentration signals from NEE and fossil fuel CO_2 emissions is an important first step in ensuring that atmospheric methods can be applied successfully to California.

Purpose

Design a system of atmospheric concentration measurements as part of a larger strategy for monitoring CO_2 exchange in California.

Project Objectives

The LBNL researchers identified four objectives:

I. Predict temporal and spatial distributions of NEE and meteorology in the Western United States for representative time periods covering the seasonal cycle of NEE.

II. Predict temporal and spatial distributions of fossil fuel CO_2 emissions in the Western United States.

III. Predict temporal and spatial distributions of CO_2 concentration signals due to NEE and fossil fuel CO_2 emissions inside and outside California.

IV. Use the atmospheric CO_2 concentration signals predicted for existing and potential future monitoring stations to judge the suitability of these stations for quantifying NEE within California.

Key Results

- The predicted atmospheric CO_2 concentration signals from NEE at many locations within California are both measurable with existing methods and often comparable or significantly larger than signals from fossil fuel emissions.

- The predicted CO_2 concentrations at marine buoys and coastal stations are significantly affected by terrestrial signals and cannot be used to represent global background CO_2 concentrations without thoughtful correction.

- A combination of existing terrestrial sites (including flux measurement sites and tall communication towers) would likely be effective as observation stations for separating CO_2 concentration signals from NEE within California from signals attributable to fossil fuel emissions and NEE outside California.

- Identification of a protocol for measuring gas concentrations that contribute to the estimation of net ecosystem exchange, with regional specificity and in the presence of combustion-related GHGs.

Project Recommendations

CO_2 Observing Stations, Sampling Frequencies, and Measurement Protocol

- New terrestrial sites sensitive to California NEE: New terrestrial observation stations should be deployed, likely on existing communications tall towers in California where signals are predominantly influenced by NEE or fossil fuel CO_2 emitted within California.

- Sampling frequency: Automated air sampling should be conducted continuously, to accurately capture the concentration during the well-mixed afternoon period and the diurnal variation. Data should be collected and averaged into approximately 30-minute intervals for further analysis. However, if resources are limited, periodic sampling with National Oceanic and Atmospheric Administration's (NOAA) flask sampling systems[5] could capture day-versus-night differences, which would provide valuable initial data to test the model predictions from this and other studies.

- Measurement protocol: Air sampling and analysis, instrument design, calibration, and analysis should follow established methods to ensure accuracy and minimize systematic errors. Continuous measurements should be checked against measurements with NOAA flask systems. In addition to the CO_2 data, standard ancillary meteorological data (e.g., temperature, relative humidity, wind velocity) should also be gathered and recorded.

- Additional stations: Observations are planned for a variety of platforms to monitor background air entering California for carbon cycle and air quality purposes. These observations will likely include the three planned marine stations planned by NOAA, periodic aircraft profiling planned by NOAA, and sampling from one or more mountaintop stations. It is also expected that existing flux measurement sites will be augmented with accurate and precise CO_2 concentration measurements. These data sets should be included in future analyses.

Uncertainty Analysis and Station Optimization

- Future work should expand on the study described in this report to predict the uncertainty that will likely be obtained in estimating the total NEE from inside California from the measured concentration data.

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[5] NOAA conducts routine sampling and laboratory analysis of air samples using standardized methods. See www.cmdl.noaa.gov/ccgg/flask.html.

- Each of the major sources of uncertainty (e.g., spatial coverage of stations, background subtraction, and transport error) should be quantified in terms of uncertainty in estimating NEE.

- Future simulations should include several complete annual cycles to sample different weather patterns and to capture interannual variations in NEE.

Measurement of Additional Trace Gas Species

- Where possible, carbon monoxide (CO) measurements should be included with CO_2 measurements to quantify fossil fuel CO_2 emissions. The use of other sources of CO (and other pollutant) data from the California Air Resources Board (CARB) might play a valuable part in this effort, particularly near urban areas where pollutant concentrations are high enough to be clearly detected with available instruments.

- Because fossil fuel CO_2 contains no radiocarbon (^{14}C), measurements of $^{14}CO_2$ in atmospheric samples can be used to infer the fraction of CO_2 due to fossil fuel combustion. Because of the high cost for precision analysis, this technique can probably only be applied with a low sampling frequency.

- The use of radon gas (^{222}Rn) as a tracer of atmospheric mixing should be explored for use in combination with CO_2 measurements to quantify net regional CO_2. This technique may be well suited to the problem of California carbon budgets, because much of the air entering California is of marine origin and will be depleted in ^{222}Rn.

Data Synthesis

- A crucial aspect of monitoring California's CO_2 emissions using the concentration measurements in an inverse or "top-down" approach will be to sensibly incorporate "bottom-up" information (e.g., ecosystem production from forest inventories and crop yields, fossil CO_2 emissions from improved inventory methods, eddy covariance CO_2 flux data from towers and aircraft flights, and ecosystem models of CO_2 exchange). This approach is an emerging area and developments in the North American Carbon Program (NACP) will be valuable to addressing these issues in California.

Estimating Non-CO_2 GHG emissions

- The methods that the LBNL researchers have applied here could be used to develop a measurement strategy for non-CO_2 GHGs. Because the relative uncertainties for fluxes of non-CO_2 GHGs are considerably larger than for CO_2, atmospheric budget and inverse approaches may be particularly effective in significantly reducing those uncertainties if atmospheric observations can be performed.

Anticipated Benefits for California

This work benefits California electricity ratepayers by providing the foundation for a network of atmospheric monitoring sites that will enable researchers to more precisely identify the CO_2 contributions from ecosystem processes and fossil fuel combustion to global warming. The resulting tool will enable the quantification and verification of net CO_2 emissions, strategies for within-state carbon sequestration, and emissions trading. This project addresses state and national needs for reliable quantification of terrestrial sources and sinks of carbon cycle gases. Ultimately, California ratepayers will benefit from more-informed greenhouse gas policies developed by California decision makers.

1.0 Introduction

1.1. Background and Overview

The Intergovernmental Panel on Climate Change (IPCC) concluded that anthropogenic increases in atmospheric greenhouse gas (GHG) concentrations are affecting global climate (IPCC 2001). In California and the Western United States, recent work indicates that the future quality of environmental services may be compromised by changing climate (Wilkinson et al. 2002; Hayhoe et al. 2004). In response, the California Energy Commission (Energy Commission) has identified quantification of California's net GHG emissions as a research priority. As such, the dominant sources of CO_2 emissions from fossil fuel combustion for electricity generation and transportation will be considered in the context of California's total GHG balance. This balance includes contributions from fossil fuel emissions and terrestrial net ecosystem exchange (NEE), both of which are expected to be affected by climate and land use.

Net ecosystem exchange is difficult to quantify on regional scales, because: (a) the drivers (e.g., climate, land use, and management) are hard to quantify; (b) estimates of gross respiratory and photosynthetic CO_2 exchanges are uncertain; and (c) measurements of these exchanges are difficult and expensive to make. Currently, the Energy Commission estimates CO_2 emissions using accounting data for fossil fuel emissions and a combination of inventory surveys and empirical models for NEE (Franco 2002). Inventory and simple budget methods are in place to estimate some stocks of ecosystem carbon pools (e.g., aboveground plant biomass, litter, and soil organic carbon) in some locations. However, it is difficult to quantify statewide carbon sources or sinks from changes in stocks because it is expensive to study large areas in sufficient detail and because large uncertainties result from calculating NEE as the difference of large and uncertain stocks. For example, recent work found large inconsistencies between carbon fluxes estimated using U.S. Department of Forestry data in Franco (2002) and fluxes estimated using data provided by the California Department of Forestry (Winrock 2004).

At the national level, the carbon cycle community was posed with the same problem of providing defensible estimates of net CO_2 (and other GHG) exchange. In response, the research community suggested the North American Carbon Program (NACP) to provide a robust approach to estimate exchange of CO_2 and other carbon cycle GHGs on regional to continental scales (Wofsy and Harris 2002) (www.esig.ucar.edu/nacp/). Similar efforts are under way in Europe (www.bgc-jena.mpg.de/public/carboeur/). The NACP is envisioned to combine inventory methods of biosphere carbon stocks and fossil fuel emissions, direct CO_2 flux measurements, and atmospheric monitoring of CO_2 concentrations, all coupled with inverse analysis employing ecosystem-atmosphere models of NEE and atmospheric transport. Atmospheric measurements facilitate independent and complimentary approaches to estimating NEE. Micrometeorological methods (e.g., eddy covariance flux) are now employed in networks of ground-based towers to directly measure long-term NEE on plot scales (~ 1–10 km) (Baldocchi et al. 2001) and aircraft-based platforms are used to directly measure short-term NEE on regional scales (10–100 km) (Desjardins et al. 1997). At present, techniques for estimation of seasonal to inter-annual NEE on larger regional scales (~ 100–1000 km) are being

6

developed. Some of these include mixing models using a tracer with a known source emission rate (Biraud et al. 2000; Biraud et al. 2002) and atmospheric boundary layer budgets based on assumptions of average dynamics in the atmospheric boundary layer (Lloyd et al. 2001; Bakwin et al. 2004; Helliker et al. 2004). As part of NACP, ambitious attempts are now under way to refine inverse techniques originally developed to estimate NEE on global to continental scales (Ciais et al. 1995; Denning et al. 1996a,b; Gurney et al. 2002).

A key feature of the inverse approach is to use NEE predicted by land surface models as an a priori estimate of NEE, which is then refined so as to minimize the difference between predicted and observed atmospheric CO_2 concentrations to produce an a posteriori estimate of NEE. This approach requires a model of atmospheric transport to relate surface fluxes of CO_2 to atmospheric concentrations of CO_2. The value of this approach is that the uncertainties in the a priori NEE, the transport model, and the measured CO_2 fluxes and concentrations can be propagated through the analysis to estimate uncertainty in the a posteriori NEE estimate. By comparing the a priori and a posteriori uncertainties in NEE, one can judge whether the atmospheric inversion approach has been effective in improving (reducing uncertainty of) the NEE estimate.

Several future sources of atmospheric data will aid the development of regional estimates. First, the National Oceanic and Atmospheric Administration's (NOAA) Climate Monitoring and Diagnostics Laboratory (NOAA-CMDL) has plans to expand their existing operations (www.cmdl.noaa.gov/publications/annrpt27/) to include additional ground-based sites and vertical profiles of CO_2 and other trace gases using aircraft. Second, in 2003, NASA approved the Orbiting Carbon Observatory (OCO). Orbiting Carbon Observatory, planned for a 2007 launch, is designed to provide column-integrated measurements of atmospheric CO_2 with ~ 1 part per million (ppm) accuracy on 10 km swaths separated by roughly 100 km on a 16-day repeat cycle (Crisp et al. 2004). The global coverage and temporal resolution afforded by OCO will be unique, although the coverage will be sparse at regional scales and the column-integrated signals are significantly smaller than those obtained from surface stations (Olsen and Randerson 2004). Hence, despite these advances, no current plans include atmospheric CO_2 concentration measurements specifically designed to enable accurate estimation of California's net CO_2 exchange.

Measurement of CO_2 concentration gradients on regional scales is challenging because the spatial gradients are small. In a simplification that aids discussion, the difference in atmospheric concentration ΔCO_2 (ppm) between two towers can be expressed in terms of the average surface rate of net exchange <NEE> (μmol m^{-2} s^{-1}) as

$$\Delta CO_2 \text{ (ppm)} = <NEE> \ L / (\rho \, u \, h), \hspace{3cm} (1)$$

where L (km) is the tower separation (km), ρ is the molar density of air (~ 40 mol m-3), u (m s-1) is the mean wind speed, and h is the height of the mixing layer (km).

For example, ΔCO_2 /<NEE> ~ 1 ppm / (μmol m-2 s-1) for a tower separation, L= 200 km, mean wind, u = 5 m s-1, and mixed layer height, h = 1 km. LBNL notes that for a tower separation, L = 200 km, an air parcel moving over the landscape at 5 m s-1 has a transit time between towers of 12 hours, or half a day. Because the average uptake over a daytime period is likely to be only -1 to -10 μmol m-2 s-1, the differences in CO_2 concentration are 1 to 10 ppm. Measuring the 1 ppm to 10% precision requires relative instrument accuracy of 0.1 ppm. This accuracy can be accomplished from the instrument perspective, because the state-of-the-art in measurement accuracy is approximately 0.1–0.2 ppm (Bakwin et al. 1998). High accuracy is necessary because an average annual flux of just 0.1 μmol m-2 s-1 is equivalent to a change of 0.38 tC ha-1 yr-1. Hence, a careful examination of the expected signal levels is an important first step in determining whether inverse methods could be successfully applied to California.

1.2 Project Goal and Objectives

The goal of this project is to design a set of atmospheric concentration measurements as part of a larger strategy for monitoring CO_2 exchange in California. This project's researchers identified four objectives to meet this goal:

- Predict temporal and spatial distributions of NEE and meteorology in the Western United States for representative time periods covering the seasonal cycle of NEE.

- Predict temporal and spatial distributions of fossil fuel CO_2 emissions in the Western United States.

- Predict temporal and spatial distributions of CO_2 concentration signals due to NEE and fossil fuel CO_2 emissions inside and outside California.

- Use predicted atmospheric CO_2 concentration signals to identify existing and potential future monitoring stations for suitability in characterizing and separating NEE within California from other sources.

1.3 Report Organization

Section 2 of this report describes the project approach. Section 3 describes the results, including spatiotemporal NEE distributions (Section 3.1); spatiotemporal fossil fuel CO_2 emission distributions (Section 3.2); spatiotemporal distributions of atmospheric CO_2 concentrations (Section 3.3); and identification and evaluation of observing stations (Section 3.4). Section 4 presents conclusions and recommendations for choosing observation stations and applying measurement protocols that provide effective augmentation of other existing and planned atmospheric monitoring efforts.

2.0   Project Approach

This section describes the methods that LBNL used to address each of the objectives described above.

2.1.   Prediction of NEE and Meteorology

The LBNL researchers predicted NEE and regional meteorology using a modeling framework (MM5-LSM1) that includes a coupled version of the PSU/NCAR mesoscale model MM5 (Grell et al. 1995) and LSM1 (Bonan 1996). The coupled model was chosen because it provides consistent predictions of NEE and surface energy fluxes (latent and sensible heat) that drive atmospheric mixing. This section describes the coupled model and how it was employed for this work.

MM5 is a mesoscale meteorological model that is used for forecasting regional-scale weather and for studying atmospheric dynamics and pollutant dispersion (for a partial list of papers see: www.mmm.ucar.edu/mm5/Publications/mm5-papers.html). The model can be run with nested grids so that large-scale atmospheric features can be captured as well as impacts of fine-scale topography and surface fluxes.

LSM1 is a land-surface model that simulates CO_2, water, and energy fluxes between ecosystems and the atmosphere. Twenty-eight land cover types are simulated in the model, each with a specified seasonality for leaf area and parameters controlling soil CO_2 flux to the atmosphere. Photosynthesis and ecosystem respiration are calculated at each time step using the land cover information and calculated meteorology in each pixel. LSM1 has been tested in a range of ecosystems at the site level (e.g., (Bonan 1995; Bonan et al. 1997; Riley et al. 2003)).
The integration of LSM1 with MM5 was accomplished via the established interface for the Oregon State University land surface model (OSULSM), with changes in the interface to account for partitioning shortwave radiation between diffuse and direct components (Chen and Dudhia 2001). Previous work has shown that the coupled model's predictions of energy fluxes, near-surface air temperatures, and soil moisture and temperature compared favorably to data collected during a previous field campaign (Betts et al. 1998; Cooley et al. 2004).

Researchers performed four simulations covering the first 15 days of March, June, September, and December of 2003. Although a full year was not simulated due to computational constraints, these periods represent a realistic range of meteorological conditions and ecosystem CO_2 exchanges over the year. The model was run with two nested grids with horizontal resolutions of 60 km over the entire United States, and 20 km over the modeling shown in Figure 1. The vertical resolution in both grids was 18 logarithmically spaced vertical layers between the surface and 20 km altitude. The following physics packages were used in the simulations: Grell convective scheme, simple ice microphysics, MRF Atmospheric Boundary Layer (MRF ABL) scheme, and the Community Climate Model (CCM2) radiation package (www.mmm.ucar.edu/mm5). LBNL used the standard initialization procedure for MM5v3.5, which applies first-guess and boundary condition fields interpolated from the National Center

for Environmental Prediction (NCEP, www.ncep.noaa.gov/) reanalysis data (Kalnay et al. 1996; Kistler et al. 2001) to the outer computational grid.

To improve the accuracy of the seasonal cycles of carbon exchange across the different ecosystem types, the research team compared the predicted NEE with results of eddy covariance flux measurements made in the Western United States and available through the FLUXNET data archive (http://daacl.esd.ornl.gov/FLUXNET/) and archival literature (Goldstein et al. 2000; Baldocchi et al. 2001; Falge et al. 2002; Law et al. 2002). Because there are relatively few sites for flux measurements compared to the large number of ecosystem types present in the Western United States, the research team aggregated the land cover types present in LSM1 into a subset of seven cover types shown in Figure 1. The team then calculated the mean NEE for each cover type using the results of this project's model runs, with the exception of the desert and urban cover types, which are parameterized to not contain photosynthetically active vegetation or soil respiration in the simplified land surface parameterization used in the model. In the cases where the calculated mean NEE is significantly different from the annual mean flux reported for that cover type, researchers scaled the daytime and nighttime exchange separately by constant factors for each of the four seasons, so that the daytime and nighttime NEE matched the diurnal cycle from the measurements and the annual mean NEE matched the FLUXNET estimates. This approach is similar to previous work where the prediction of photosynthesis is assumed to be correct, but soil respiration of CO_2 is scaled by a constant factor in each pixel to produce zero net annual CO_2 exchange (Denning et al. 1996a). The LBNL method differs from that approach in that researchers used field measurements to determine the mean annual carbon balance in a given cover type and did not require that individual pixels were in carbon balance. This project's researchers believe this is appropriate because many California ecosystems are managed to accomplish a net removal of CO_2 from the atmosphere (e.g., timber forestry and crop agriculture). In this project's approach, researchers calculated the annual mean NEE and also the mean NEE for daytime and nighttime in each season from the measurements. If the model predictions of mean annual NEE averaged over a given cover type was significantly different from the mean calculated from field measurements, then researchers scaled NEE in all pixels of that cover type by a constant factor, so that both the annual mean and the mean daytime and nighttime NEE matched the field measurements.
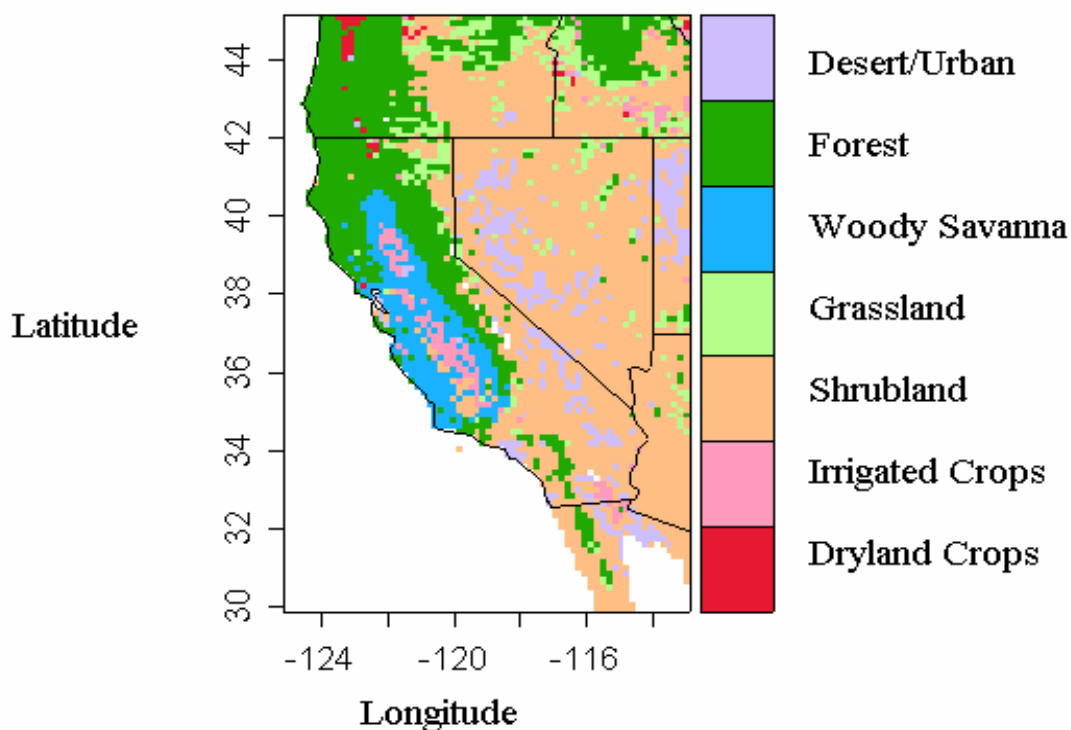
Figure 1. Vegetation distribution used to characterize land cover in the Western United States for the simulations described in this report. The pixel size is 20 km on a side.

2.2. Prediction of Fossil Fuel CO_2 Emissions

The research team predicted the spatial and temporal distributions of CO_2 from fossil fuel emissions in the Western United States by scaling estimated emissions of other combustion-related pollutants (e.g., carbon monoxide (CO) and nitrogen oxides(NO_x)) that have been shown to correlate with atmospheric CO_2 concentrations (Potosnak et al. 1999; Dillon et al. 2002; Gerbig et al. 2003; Lamarque and Hess 2003). The team used CO data reported in the U. S. Environmental Protection Agency's (EPA) National Emission Inventory (NEI) of criteria pollutants (EPA 2001). Researchers obtained the NEI database from the Lake Michigan Air Directors Consortium (LADCO), on a grid with 36 km resolution for the continental United States. The database contained hourly emissions for weekdays, Saturdays, and Sundays of each month in 1999. The team extracted the CO data from the NEI and interpolated it to produce maps at 20 km resolution. Fossil fuel CO_2 emissions were calculated by multiplying CO emissions by a constant factor of 23.3, so that the annual sum of surface CO_2 emissions matched the Energy Commission's estimate of California CO_2 emissions in 1999 (363 millions of tons of CO_2 (Mt CO_2) minus approximately 17 Mt CO_2 for bunker and aviation fuel combustion)

11

(Franco 2002). This scaling factor is reasonably consistent with previous work on atmospheric CO_2:CO ratios attributed to signals from fossil fuel combustion (Potosnak et al. 1999).

This method provides a high-resolution picture of fossil fuel CO_2 that is sufficient for this planning exercise. However, before using this type of information in an inverse analysis, refinements in the modeling should address the following issues. First, although the fossil CO_2 emission maps likely capture the dominant spatial and temporal features of the CO_2 emissions, they will contain regions and periods for which the CO_2:CO ratio varies (e.g., high CO from biomass burning or low CO from natural-gas-fired electricity production). A superior approach would be to use the information on fuel use underlying pollutant emissions to estimate CO_2 directly. Second, as mentioned above, these fossil fuel CO_2 emissions do not contain bunker or aviation CO_2 emissions from marine or aircraft transportation. These emissions can be included with some consideration of their spatial distribution in the atmosphere. Third, the predictions should use an emission inventory specific to the year being simulated or be adjusted appropriately.

2.3. Prediction of Concentration Signals

LBNL predicted atmospheric CO_2 concentrations using the EPA Community Multiscale Air Quality (CMAQ) model (www.epa.gov/asmdnerl/models3/doc/science/science.html). CMAQ was developed and applied for modeling air quality, incorporating the processes of bulk air motion, turbulent diffusion, and thermal and photo-chemistry (EPA 1999; Cohn et al. 2001; Bullock et al. 2002). Spatially and temporally resolved surface emissions were input to the model. Meteorological inputs were taken from the MM5 model predictions that included wind vectors, atmospheric boundary layer (ABL) height,[6] and vertical velocity fluctuations to compute the motion of air parcels.

CMAQ was used to calculate the temporal and spatial propagation of atmospheric CO_2 with the only sources and sinks occurring at the land surface, as prescribed by the maps of NEE and fossil fuel CO_2 emissions. This is valid because CO_2 is neither generated nor lost through chemical reactions in the atmosphere. Initial and boundary conditions for CO_2 concentrations were set to a constant value of 370 ppm and signals were calculated with respect to this background. LBNL subdivided NEE and fossil fuel CO_2 into in-state and out-of-state components and then calculated the CO_2 signals from four sources of surface flux: (1) NEE within California (NEE.in), (2) NEE outside California (NEE.out), (3) fossil fuel CO_2 from combustion inside California (ffCO2.in), and (4) fossil fuel CO_2 from combustion outside California (ffCO2.out).

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[6] *ABL height* is the height in the atmosphere to which air is well mixed.

2.4. Identification and Evaluation of Observation Stations

The LBNL team identified an initial set of surface observation stations by starting with existing carbon cycle monitoring networks (e.g., NOAA-CMLD; www.cmdl.noaa.gov, and the Ameriflux Program http://public.ornl.gov/ameriflux). However, because of their relatively sparse coverage, this project included two categories of other stations. Some of the additional stations were marine buoys planned by NOAA for offshore monitoring. Others were obtained from lists of radio and television transmission towers (http://wireless2.fcc.gov/UlsApp/AsrSearch) similar to the Park Falls Tower in Wisconsin where CO_2 measurements have been made previously (Bakwin et al. 1998).

The team evaluated the efficacy of these observing stations by examining the time series concentration signals obtained at each station from the four component sources (NEE.in, NEE.out, ffCO2.in, and ffCO2.out). Three criteria were used in the selection process. First, researchers wanted to identify marine stations that had only small signals from the terrestrial sources. These stations would be used to quantify the CO_2 concentration boundary conditions for air entering the region. Second, the team wanted to find stations that provided measurable signals from terrestrial sources. Researchers used the time series data to calculate the mean mid-day signals from each component source and over each season. Mid-day CO_2 concentration signals were chosen because the mixing height of the atmospheric boundary layer is generally well defined and, although large, can be accurately represented in meteorological models. By comparison, nighttime atmospheric mixing is often poorly defined and represented. Third, LBNL wanted the signals from NEE.in at the stations to be clearly distinguishable from signals attributable to the other sources. To quantify the degree of similarity between signals, researchers calculated the covariance between the signal from NEE.in and the signals from each of the other three sources. If there was little covariance, then signal variations attributable to NEE.in could be measured, and the signals from other sources would add noise (but not bias) to the measurement.

3.0 Results and Discussion

3.1. Spatiotemporal Distribution of Net Ecosystem Exchange

Using the coupled MM5-LSM1 simulations, the LBNL team predicted regional meteorology and NEE for the Western region over the first 15 days of March, June, September, and December. Researchers calculated the average NEE for each cover type over the four periods of the study. Both the mean NEE for forest (-0.66 t C ha^{-1} yr^{-1}) and for shrub lands (0.38 t C ha^{-1} yr^{-1}) were close to carbon balance, and reasonably consistent with the range of estimates for the annual NEE from the literature (Goldstein et al. 2000; Baldocchi et al. 2001; Falge et al. 2002; Law et al. 2002). The mean NEE of irrigated crops (–10.5 t C ha^{-1} yr^{-1}) and dry crops (–5.5 t C ha^{-1} yr^{-1}) both showed the large net uptake expected from managed agricultural systems, where nitrogen is applied and crop residues are removed after harvest. The predicted mean NEE of woody savanna (-19.5 t C ha^{-1} yr^{-1}) and grassland (–6.2 t C ha^{-1} yr^{-1}) were sufficiently different from values observed in California oak woodland (pers. comm. D. Baldocchi) and grassland systems

13

(Xu et al. 2004) that adjustments were made to reduce net daytime uptake and increase net nighttime release as described in Section 2.1. The resulting mean NEE of woody savanna and grassland were both -0.7 t C ha^{-1}yr^{-1}.

Predicted NEE exhibits large variations, both in time and with cover type. For example, the maps in Figure 2 (and Figure A1 in Appendix A) show the diurnal variation in NEE over the course of a day in June. As expected, nighttime NEE is positive, reflecting plant and soil respiration of CO_2 to the atmosphere. Daytime NEE is negative for ecosystems that are actively assimilating CO_2 from the atmosphere (e.g., forest, woodland, and crop lands), but slightly positive for shrub ecosystems where, on this day, respiration was larger than photosynthesis. The large spatial variations in NEE reflect the varied ecosystems present in California. Similarly, the ecosystems have different seasonality, which generates seasonal NEE patterns (see figure A2 in Appendix A). Capturing these seasonal NEE variations is important in order to accurately predict seasonal variations in atmospheric CO_2 concentrations.
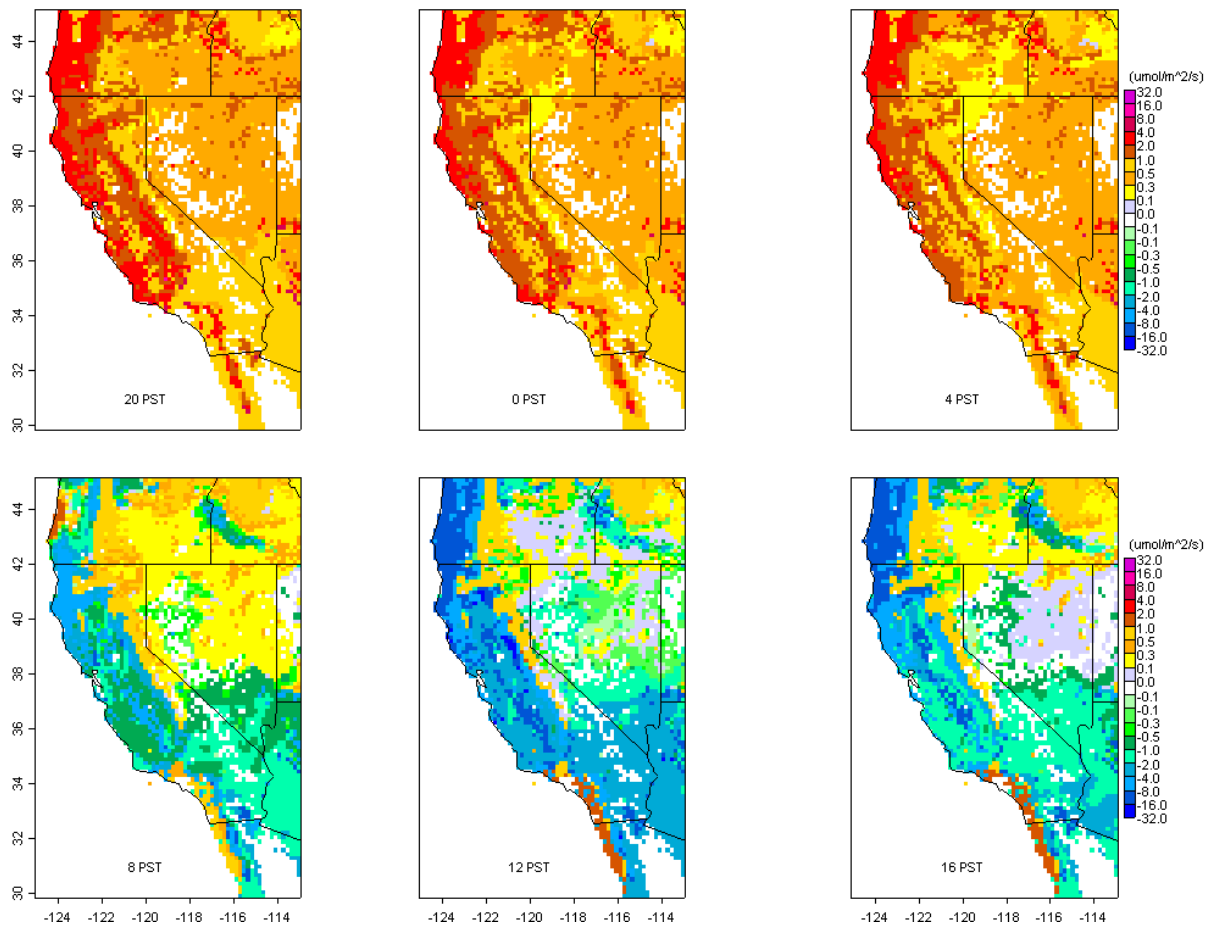
Figure 2. Maps showing the diurnal cycle of predicted net ecosystem exchange, NEE (μmol CO$_2$ m-2 s-1), for a day in June. Horizontal and vertical axes are longitude and latitude, respectively. Upper panels show that positive fluxes to the atmosphere dominate at night, due to respiration. Lower panels show that negative fluxes to the atmosphere dominate during the day, when photosynthesis removes CO$_2$ from the atmosphere. Note: NEE is shown with a logarithmic scale.

3.2. Spatiotemporal Distribution of Fossil Fuel CO₂ Emissions

Figure 3 shows a representative diurnal cycle of CO_2 emissions from fossil fuel combustion in the Western United States, for a weekday in June. As expected, fossil fuel CO_2 emissions were strong in large urban centers (larger than any positive ecosystem fluxes), but were spatially localized. Away from urban centers, emissions remained significant only along suburban transportation corridors. Emissions from aircraft and ship traffic were not included, but represent a small fraction of estimated CO_2 emissions from California. The temporal variations in fossil fuel CO_2 fluxes were much smaller than temporal variations in signals from NEE because ecosystems have distinct diurnal and seasonal cycles of net uptake and release. Given that the temporal variations in CO_2 concentration signals from fossil fuel CO_2 are smaller than the variations from NEE, this project's researchers hypothesize that fossil fuel signals could be predicted and subtracted from measured signals to yield the signal from NEE. This hypothesis should be investigated in future work.
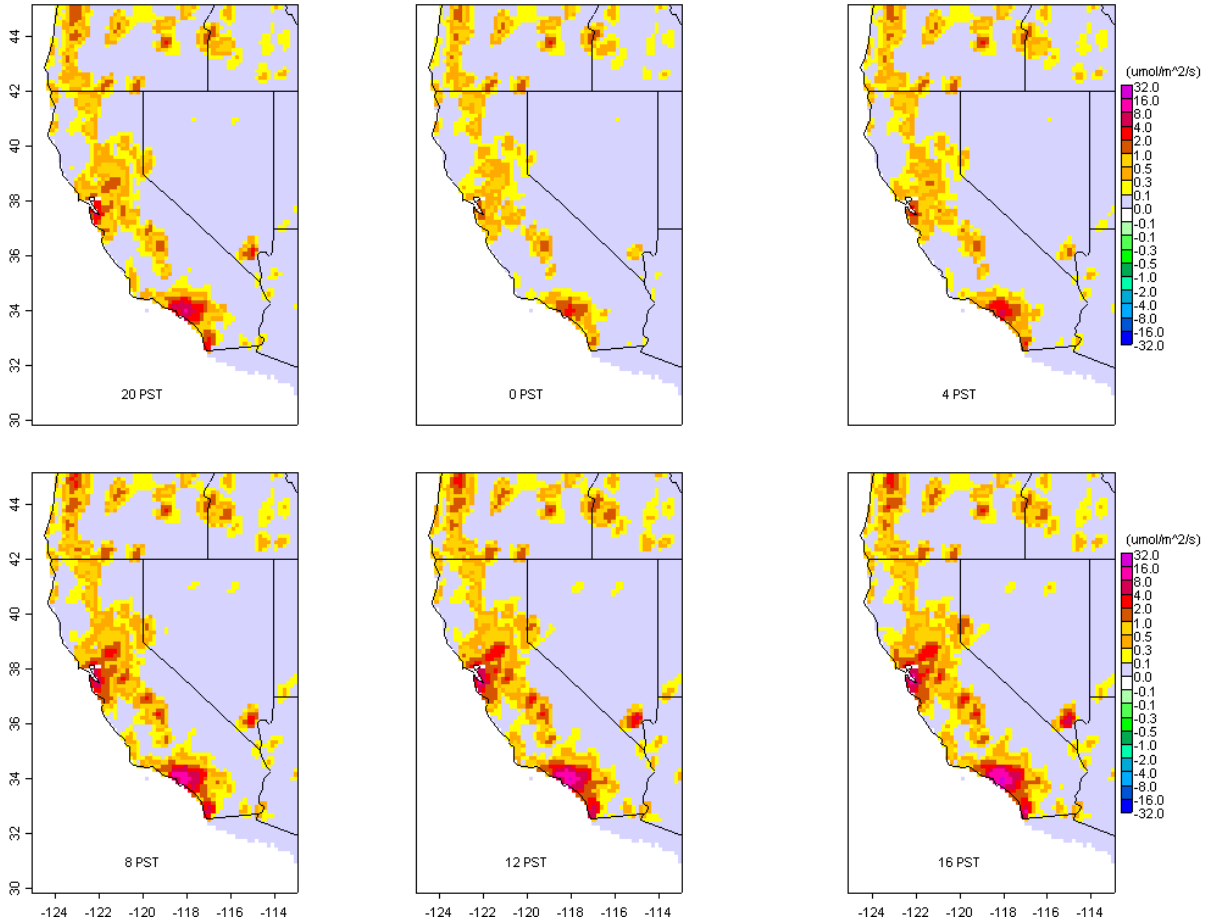

Figure 3. Maps showing the diurnal cycle of estimated fossil fuel CO₂ emissions for the Western United States for a weekday in June. Panel layout, axes, and logarithmic scale for units are the same as in Figure 2.

15

3.3.   Spatiotemporal Distribution of CO_2 Concentrations in the Atmosphere

Atmospheric CO_2 concentrations were predicted for the four simulation periods using predicted NEE, fossil fuel CO_2 emissions, and meteorology described above. All CO_2 concentrations are reported as deviations from the constant boundary condition applied at the edge of the simulation domain. Figure 4 shows the diurnal cycle in CO_2 concentration signals from NEE in the lowest (0–100 m) model layer of the atmosphere for the June day shown in Figure 2. In areas with strong surface uptake, concentrations were reduced below the background, while in areas with strong sources they increased above the background. Air parcels containing significant CO_2 concentration signals were predicted to advect to marine locations up to 300 km west of the coast, consistent with the results of another study (Riley et al. 2004). This prediction suggests that attempts to use the data from marine and coastal stations to provide boundary condition information on the air entering California will require correction for terrestrial influence. From these maps one can also conclude that the spatial differences in CO_2 signals across California are large enough to be clearly measured with available instrumentation.
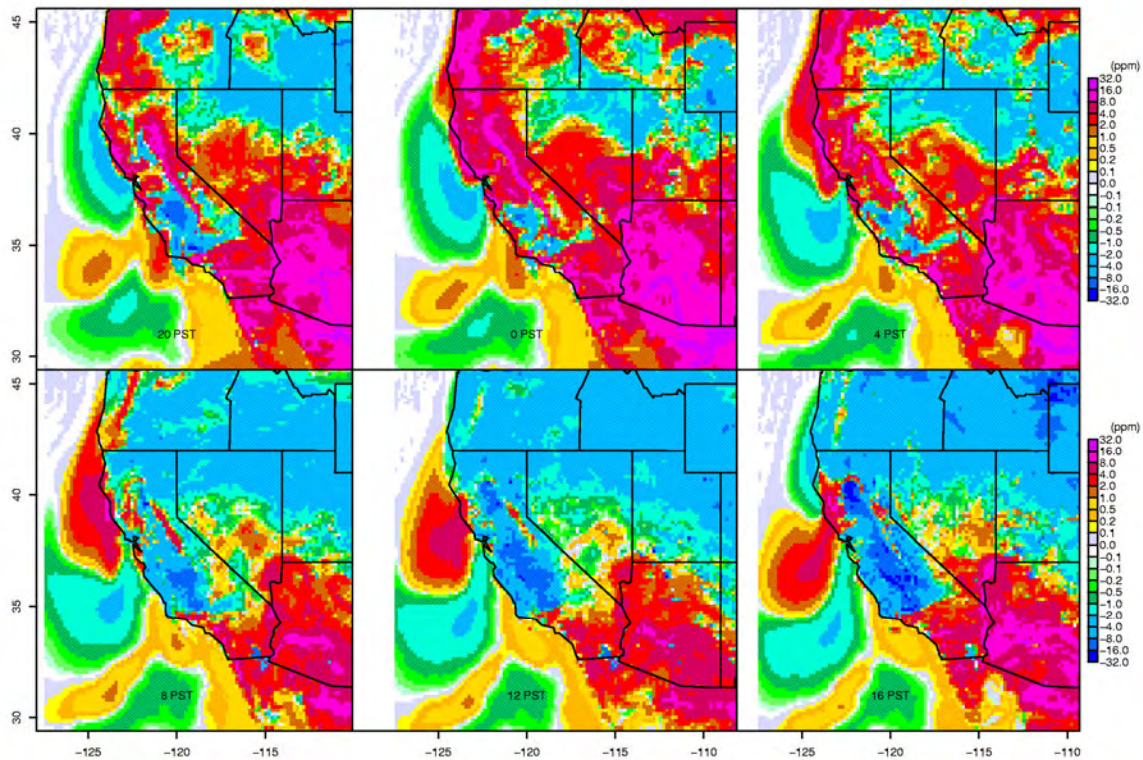
Figure 4. Maps showing diurnal variation in surface layer CO_2 concentrations resulting from NEE for the day shown in Figure 2. The upper (lower) three panels correspond to nighttime (daytime) periods. Horizontal and vertical axes are longitude and latitude respectively. Note that CO_2 concentration contours are logarithmically scaled. The spatial variations in CO_2 concentration are large enough to be clearly detected with available instrumentation.
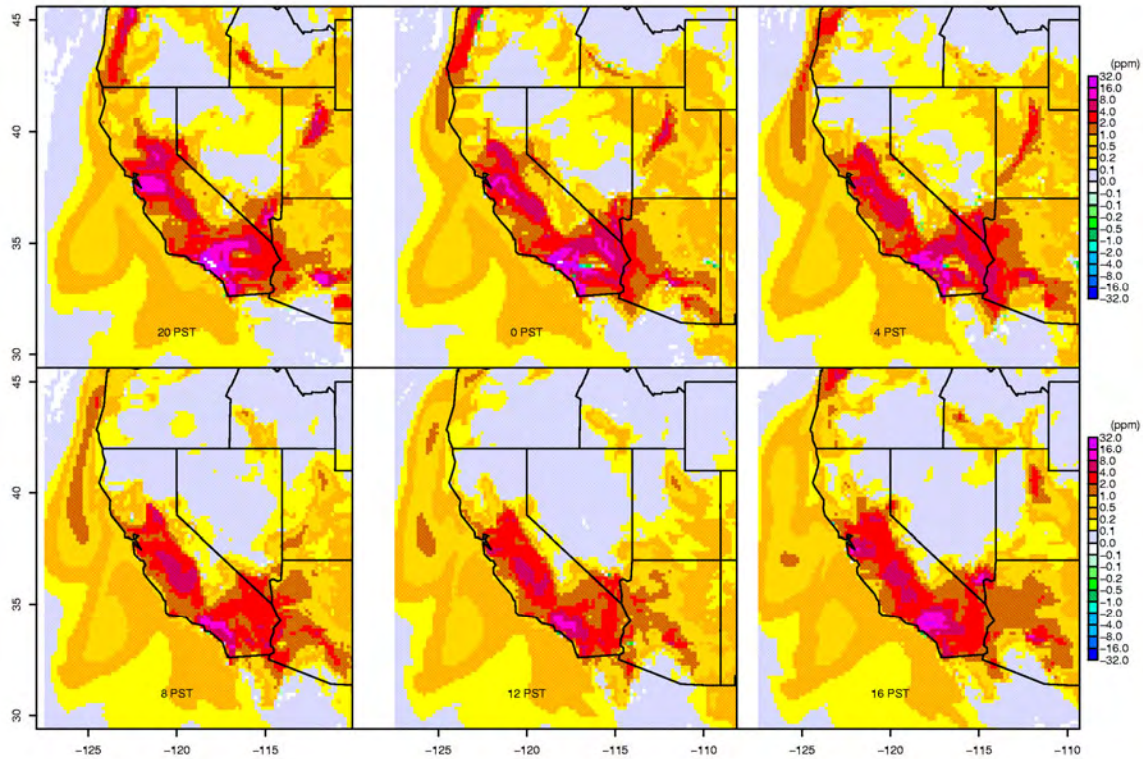
16

Figure 5. Maps of diurnal variation in surface layer CO_2 concentrations resulting from fossil fuel CO_2 emission for June time period as in Figure 4. Panel layout, axes, and logarithmic scale for units are the same as in Figure 4.

Figure 5 shows the diurnal cycle in CO_2 concentrations resulting from fossil fuel CO_2 emissions for the same period as Figure 4. In this case, only increases above background are predicted because all fluxes are positive with respect to the atmosphere. As with the emissions map, the most significant increments in CO_2 concentration occurred near the urban centers, but significant plumes of CO_2–enriched air were also transported to other locations far from that of the emissions. However, the mean and diurnal variations in fossil CO_2 signals were generally smaller than CO_2 signals from NEE at most locations away from urban centers. The smaller size and lower variability of fossil CO_2 signals suggests that subtracting predicted fossil CO_2 signals from future measurements of CO_2 concentration may be effective for estimating the signals from NEE at many locations. This increases confidence that atmospheric observations will enable effective estimation of NEE.

In order to facilitate identification of the most promising locations for observing stations, the research team calculated the CO_2 signals for four components—signals derived from: (1) NEE within California (NEE.in), (2) NEE outside California (NEE.out), (3) fossil fuel CO_2 from combustion inside California (ffCO2.in), and (4) fossil fuel CO_2 from outside California (ffCO2.out). Figure 6 shows the mean midday surface layer concentration signals for each of the four components in June. The panels of Figure 6 show that the Central Valley and Central Coast areas had negative signals from NEE inside California and positive signals from fossil

17

fuel CO_2 produced inside California. During this period, Southern California had positive signals from both NEE and fossil fuel CO_2. Coastal and marine areas obtained smaller positive signals from plumes transported off the coast. As shown in Appendix B, these patterns varied significantly with season. In the case of NEE, the patterns varied because NEE has significant seasonal variations as the result of ecology and climate. In the case of fossil fuel CO_2, the variations are driven mostly by variations in the mean meteorology for the different months.

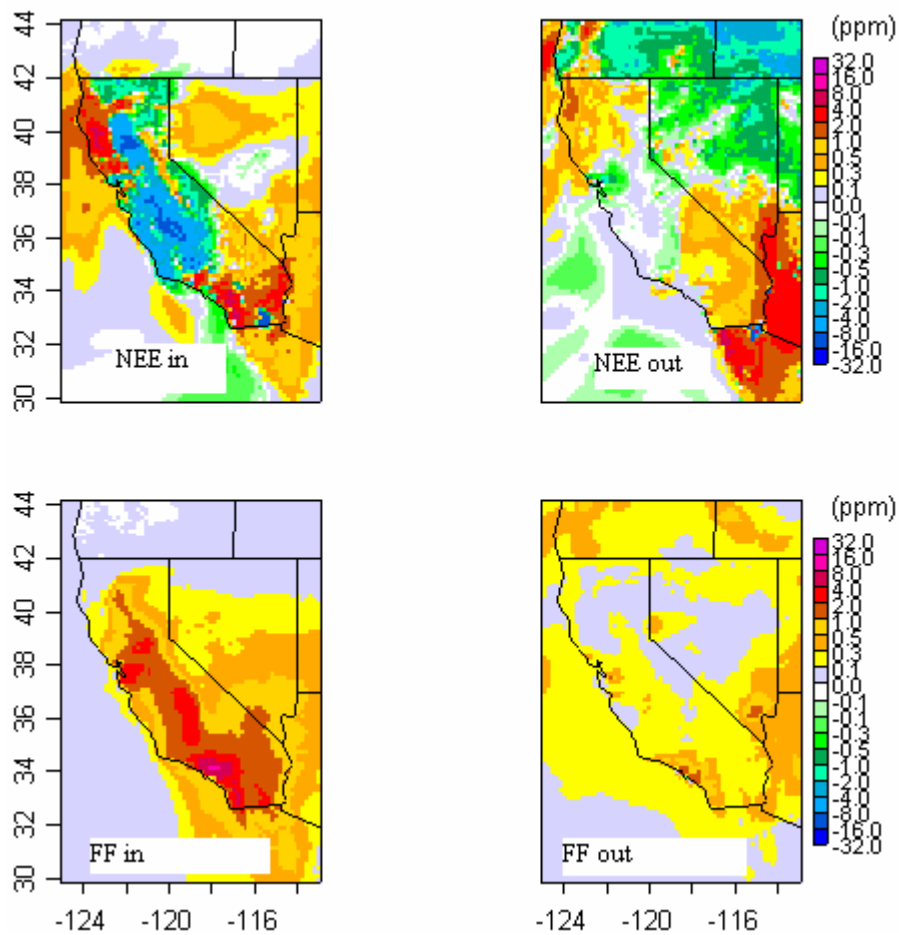**Figure 6. Maps of June midday mean surface layer CO_2 concentrations resulting from NEE inside (upper left) and outside (upper right) California, and fossil CO_2 emissions inside (lower left) and outside (lower right) California. As with previous figures, the horizontal and vertical axes are longitude and latitude, respectively. Note that CO_2 concentration contours are logarithmically scaled.**

3.4. Identification and Evaluation of Observation Stations

3.4.1. Existing and Potential Future Stations

A set of existing and potential future monitoring stations is shown in Figure 7 and Table 1. Some of the existing stations are part of the U.S. National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory (NOAA CMDL) measurement and sampling network (see www.cmdl.noaa.gov/publications/annrpt27/), some are independent sites (e.g., Scripps), and others are Ameriflux sites where accurate CO_2 measurements could be implemented, and have been at Blodgett Forest (Station 13). Note that there are other existing ecological and biogeochemical flux measurement sites in California that could be included in future analysis, but such a compilation was beyond the scope of this study. The marine stations are chosen to sample the atmosphere from relatively pristine locations that provide boundary conditions for air entering the California. The coastal stations sample air in a transition regime. The inland stations sample air that is heavily influenced by terrestrial surface fluxes. This project did not include a significant number of sites east of California because the topography of the Sierra poses a serious challenge for modeling atmospheric transport.
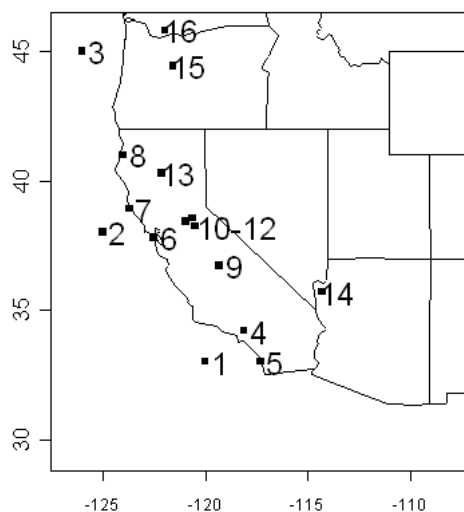

Figure 7. The positions of existing and possible future observations stations examined in this study. The locations range from marine stations that largely sample background air to inland stations that sample air subject to strong terrestrial influence.

19

Table 1. Existing and potential monitoring stations. For existing sites the name of the research program is listed in parentheses.

Station	Name	Latitude (degree)	Longitude (degree)	height above ground (m)
1	Buoy	33.000	-120.000	3
2	Buoy	38.000	-125.000	3
3	Buoy	45.000	-126.000	3
4	Tall Tower	34.200	-118.100	296
5	Scripps Pier (Scripps Inst.)	33.000	-117.300	10
6	Tall Tower	37.800	-122.500	298
7	Point Arena (NOAA)	38.911	-123.692	10
8	Trinidad Head (NOAA)	41.000	-124.000	10
9	Tall Tower	36.700	-119.300	259
10	Tall Tower	38.240	-120.502	624
11	Tonzi Ranch (Ameriflux)	38.432	-120.966	12
12	Blodgett Forest (Ameriflux)	38.550	-120.633	15
13	Tall Tower	40.300	-122.100	304
14	Tall Tower	35.700	-114.300	396
15	Metolious (Ameriflux)	44.437	-121.567	12
16	Wind River (Ameriflux)	45.821	-121.951	73

3.4.2. CO_2 concentration signals at monitoring station locations

The time series of concentration signals calculated for each station was extracted from the concentration maps and examined to determine the contributions to the predicted signals from NEE and fossil CO_2 emissions inside and outside of California. Figure 8 (and Appendix C) shows the mean midday concentration signal for each station and season. As mentioned above, researchers separated the stations into categories based on whether their primary influence was oceanic (Stations 1–3) and primarily of use for monitoring boundary conditions; coastal (Stations 4–8) and influenced by a mixture of marine and interior air; interior (Stations 9–13) and strongly influenced by NEE and fossil CO_2; or outside of California (Stations 14–16) and of value for monitoring boundary conditions. Within the station groupings, the stations are arranged from south to north.

The general patterns show increasing signals from NEE.in and decreasing signals from ffCO2.in from south to north. This is because Southern California is quite arid and does not support the high rates of ecosystem carbon exchange that are possible in the comparatively moister conditions found in Northern California. Other significant features for stations within California are consistent seasonality (also see Appendix C) with negative NEE.in signals during March; small or positive signals in June near the coast but negative signals inland (from irrigated agriculture and Sierran forests); uniformly positive signals in September when most areas are subject to water stress; and small signals in December when temperatures are lower.

Patterns for ffCO2.in and ffCO2.out show less seasonality, largely due to variations in atmospheric transport, because fossil emissions did not vary significantly with season. The signals predicted for the different stations vary by grouping and latitude. Stations 1 and 2 show mean signals of ~ 1–2 ppm with comparable day-to-day variations, suggesting that their use as background monitoring stations will require incorporating estimated terrestrial signals. Researchers note that this may also be true for Station 3; it is near the northwest edge of the modeling domain and signals from terrestrial CO_2 exchanges even farther north may influence the signal at Station 3. Stations 6–13 showed significant signals from NEE.in, while stations 4, 5, 9,11, and 12 all exhibited large signals from ffCO2.in and could be used to monitor fossil emissions. Stations 14–16 exhibited strong signals from NEE.out and ffCO2.out and would therefore provide information to estimate a combination of those sources. Finally, the signals from the tall towers (4, 6, 9, 10, 13, 14) generally exhibited smaller day-to-day variations as compared with nearby surface stations (Appendix B). This reduced variability occurs because they average over larger areas, a fact that makes them potentially superior for regional inverse studies.

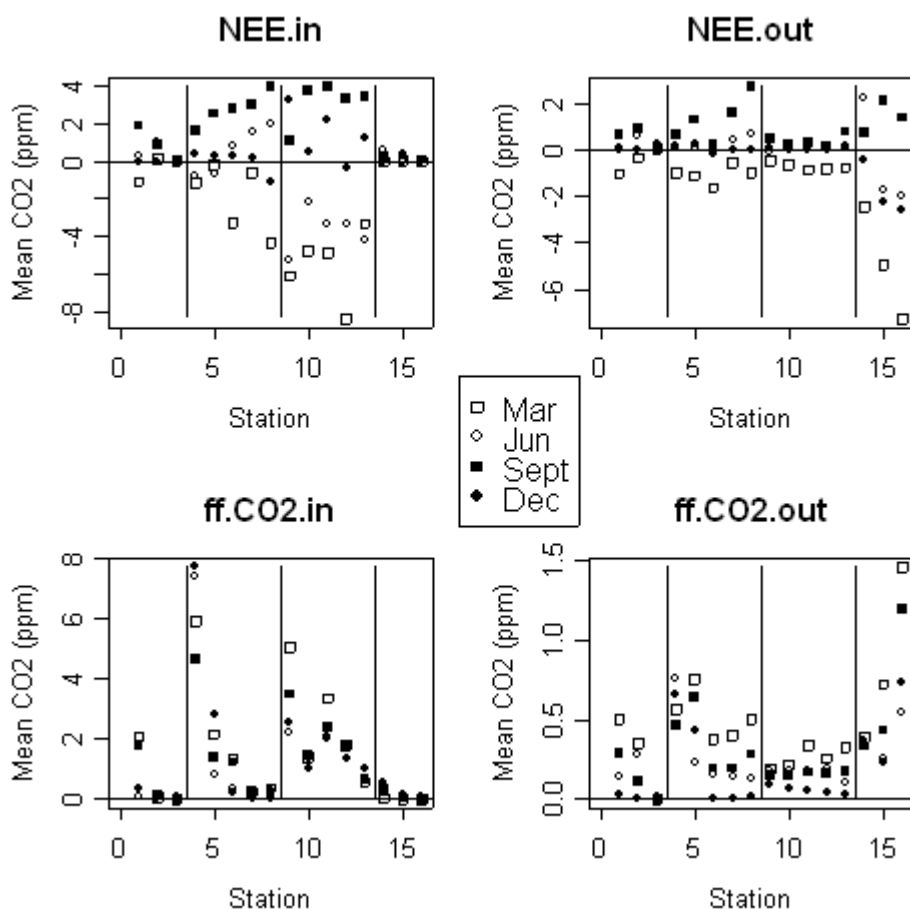**Figure 8. Mean CO_2 concentration signals from NEE in and out and fossil fuel CO_2 emissions in and out of California for each of the four months examined in this study. Vertical lines separate the stations into four groups in the following order: (1) oceanic, (2) coastal, (3) interior, and (4) interior outside California. CO_2 concentrations are deviations from the seasonal background.**

21

3.4.3. How Well Do Concentration Signals at Monitoring Sites Allow Discrimination of NEE Inside California from Other Signals?

Additional insight into the relative strengths of the observing stations can be obtained by inspecting the covariance between signals from NEE.in and the other signals shown in Figure 9. The research team normalized the covariance between signals from NEE.in and other signals by the standard deviation in signal from NEE.in. This measure shows the amount of signal variation from the other sources that are correlated with (and could not be distinguished from) variations from NEE.in. In most cases, the covarying signals were small compared to the signal variations from NEE.in. This suggests that if the variables governing variation in the signal from NEE.in can be captured in an ecosystem-atmosphere model (e.g., MM5-LSM1), then an inverse model can use the measured signals to estimate NEE.in without interference from the other signals. A subset of stations (6, 7, 8, 10, 12, and 13) did not exhibit significant signal correlations between NEE.in and ffCO2.in, and only limited correlations with NEE.out and ffCO2.out. Station 12 (Blodgett forest) appeared particularly well-suited in this respect, although modeling the transport fields for Blodgett poses a greater challenge (because of the mountainous terrain) than for the Central Valley sites. Based on these results, this project's researchers conclude that measurements made at a subset of these stations are likely to offer an opportunity to quantify NEE.in without significant interference from other sources.
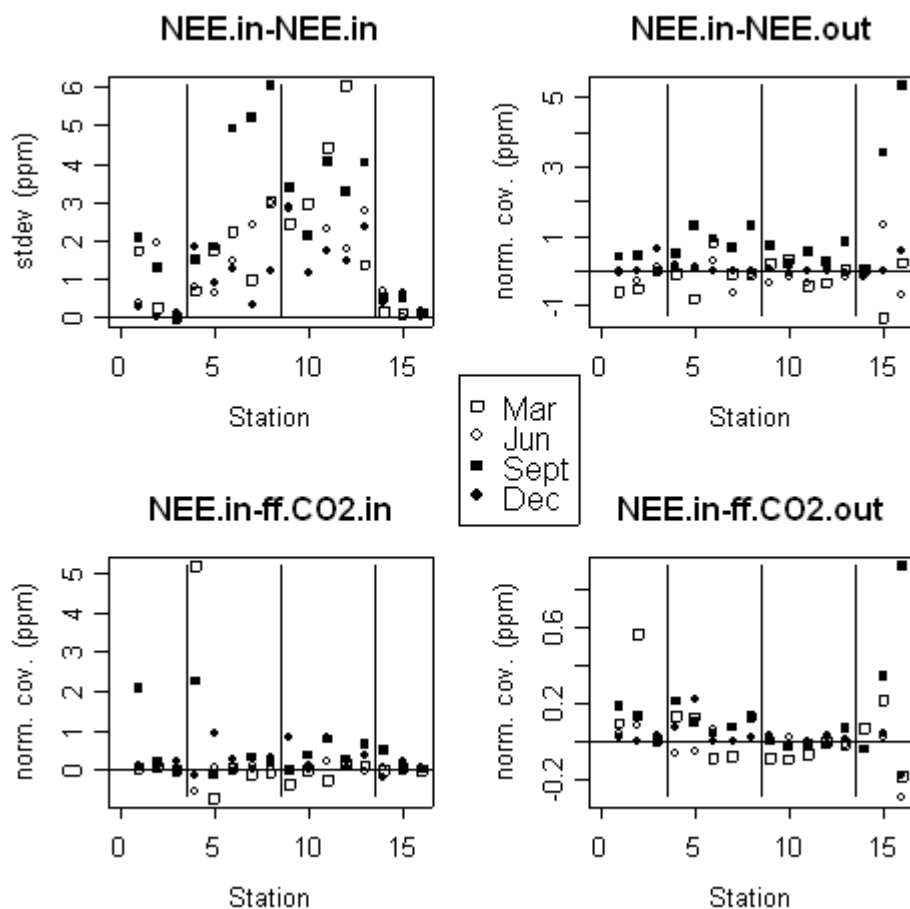
Figure 9. Standard deviation of midday CO_2 signals from NEE inside California (top left), showing predicted variation in daytime signals for each season. The normalized covariance of the signal from NEE.in with the other signals is also shown: NEE outside California (top right), $ffCO_2$ inside California (bottom left), and $ffCO_2$ outside California (bottom right). In all cases the normalization factor is the standard deviation of NEE.in, yielding the component (or projection) of each signal that is correlated with signal from NEE.in. Several stations show normalized signal covariances that are small compared to the standard deviation of the NEE.in signal are hence likely to offer an opportunity to quantify NEE.in without interference from other sources.

4.0   Conclusions and Recommendations

This section provides conclusions and recommendations for: (1) a proposed set of initial observation stations, sampling frequencies, and a measurement protocol for CO_2, (2) analysis of the uncertainties in future inverse model estimates of NEE and refinement of observing stations, (3) measurement of additional trace gases that would enhance the ability to estimate CO_2 exchange, (4) initiation of a data synthesis effort to couple data from different sources relevant for estimating NEE, and (5) application of atmospheric methods for non-CO_2 GHG emissions.

4.1.   Observation Stations, Sampling Frequency, and Measurement Protocol

The results of this project have shown that there are locations where atmospheric CO_2 measurements will help constrain California's NEE. Based on these results, this project's researchers recommend an initial sampling at a limited number of sites to provide a baseline for future efforts:

- New terrestrial stations. New observing stations should be deployed at existing communications tall towers in California, chosen so that CO_2 signals are strongly influenced by either NEE.in or ffCO2.in. Stations 4, 9, 10, and 13 are well suited in this respect. Station 4 would provide an unambiguous measure of emissions from the Los Angeles area; Station 9 would sample air in the San Joaquin Valley that is effected by a mixture of agricultural and Bay Area emissions; Station 10 would be effective for monitoring signals from NEE that are attributable to Central Valley agriculture and forests in the Sierra, with a comparatively small signal from fossil CO_2 emissions; and Station 13 would monitor exchange from northern valley agriculture and forests.

- Sampling frequency. Ideally air sampling should be conducted continuously in an automated manner to accurately capture the concentration during the well-mixed afternoon period and the diurnal variation. Data should be collected and averaged into approximately 30-minute intervals for further analysis. However, if resources are limited, periodic sampling with NOAA flask systems could be performed to provide valuable initial data to test the model predictions similar to those performed in this study.

- Measurement protocol. Air sampling, instrument design, calibration, and analysis should follow protocols established previously to ensure accuracy and minimize systematic errors. The measurement protocol is described in detail in Bakwin et al. (1995). Briefly, CO_2 concentrations should be continuously measured with high precision and accuracy. This can be accomplished with instruments based on commercially available non-dispersive infrared gas analyzers (e.g., Licor 6252 or similar) augmented with active pressure and temperature control (Bakwin et. al. 1995). Sample air should be dried before being introduced into the analyzer and residual water vapor should be monitored. Particularly, the instrument should be calibrated against multiple known standards (preferably supplied by NOAA) several times per day. Periodic

sampling with NOAA flask systems should also be performed at these sites to provide a check on the continuous measurements.

- Additional stations. Observations are planned for a variety of platforms to monitor background air entering California for carbon cycle and air quality purposes. This will likely include the three planned marine stations planned by NOAA, periodic aircraft profiling planned by NOAA for Trinidad Head and a site in Southern California, and potentially continuous or flask sampling from one or more mountaintop stations. As noted above, interpreting signals from the marine stations will require estimation of signals from terrestrial sources in North America. It is also expected that existing flux measurement sites will be augmented with accurate and precise CO_2 concentration measurements. These data sets should be included in future analyses.

4.2.   Uncertainty Analysis and Site Optimization

Because it was beyond the scope of the current work, this project did not include an analysis of the uncertainty in NEE that could be obtained using data from the suggested observing stations in an inverse approach. Before implementing a full set of observing stations, an analysis of the likely uncertainty in estimating NEE using atmospheric concentration data is warranted. In particular, one should determine whether the uncertainty in estimating NEE using the atmospheric inverse approach is very large or if an infeasible number of stations are required. This is problem is complicated because the choice of the inverse approach and multiple sources of uncertainty all affect the final uncertainty in CO_2 flux, as well as the optimal locations for a given number of stations. In particular, the desired spatial resolution of the NEE estimates will depend on the number and locations of the stations. Sources of (likely correlated) uncertainty include: (1) the *a priori* NEE estimate, (2) the meteorology and hence atmospheric transport, (3) the background CO_2 concentrations from outside the modeling domain, (4) the CO_2 contribution from fossil emissions, and (5) the uncertainty in the concentration measurements themselves. To address these issues, the research team recommends the following activities:

1. Simplify the consideration to focus on the uncertainty in estimating the total NEE from inside California. Use simplified forms (assume errors are uncorrelated) for the uncertainties from each of the five sources above, apply a Monte Carlo approach to generate pseudo data, and then estimate the distribution of California NEE obtained from applying an inverse method. Iterate this calculation with different combinations of towers or alternate locations to estimate the optimal number and location of towers, in part driven by budget considerations. This approach would probably provide a good first guess as to whether acceptable uncertainties in NEE for California could be obtained with a limited number of towers and hence whether and where to proceed with instrument deployment.

2. Improve the understanding of each of the five sources of uncertainty listed above. For example, predictions of CO_2 concentrations should include calculation of signals from the seasonally and spatially varying global background of CO_2 concentrations. First-

25

order estimates in boundary conditions could be derived from the CMDL Globalview CO_2 product (www.cmdl.noaa.gov/ccgg/globalview/index.html). These estimates should be compared with the results of aircraft campaigns that measure the vertical profile of CO_2 (and other gases) over the Eastern Pacific. Estimating the boundary conditions will also be valuable because it will allow a comparison between predicted CO_2 concentrations and those measured at existing stations.

3. Expand the time periods covered in the investigation and the spatial resolution of the inverse estimates. Include several complete annual cycles to sample different weather patterns over multiple years which capture interannual variations in both meteorology and NEE (which is strongly dependent on meteorological forcing). Investigate how well NEE from different regions within California can be separately identified.

4.3. Additional Trace Gas Species for CO_2 Source Attribution

Although it is beyond the scope of this study to analyze this problem in detail, there are several additional trace-gas species that would provide important additional constraints on CO_2 exchange:

- Carbon monoxide and certain organic compounds (e.g., acetylene (C_2H_2)) have been identified as useful tracers of combustion (Potosnak et al. 1999) and should be developed for use in California, as is currently the case at Blodgett Forest. The use of CO (and other pollutant) measurements from the California Air Resources Board (CARB) might play a valuable part in this effort, particularly near urban areas where pollutant concentrations are high enough to be clearly detected with the available instruments. If dedicated future CO_2 measurement stations are commissioned, inclusion of precise monitoring of CO (and other species) in addition to CO_2 would significantly enhance their capability (Potosnak et. al, 1999).

- Radiocarbon CO_2 ($^{14}CO_2$) can provide a strong constraint on fossil fuel combustion because the 5700 year half-life for ^{14}C is short compared to the age of geologically derived petroleum hydrocarbons, and fossil hydrocarbons contain no ^{14}C. Given the current precision and accuracy of $^{14}CO_2$ measurements, it should be possible to quantify the $^{14}CO_2$ free component of air to ~ 1 ppm. Several groups, including NOAA CMDL and Lawrence Berkeley National Laboratory, are independently initiating the use of atmospheric sampling and analysis of $^{14}CO_2$ for this purpose. Because of the high cost for precision analysis (roughly $300 per sample) this approach is currently beyond the scope of most routine monitoring programs, but might be employed to add precision to fossil CO_2 estimates during an intensive measurement period.

- The ratio of CO_2 to ^{222}Rn has been used to estimate net regional CO_2 exchange using the assumption that surface emission rate of ^{222}Rn can be accurately determined (Biraud et al. 2000; Biraud et al. 2002). This technique is well suited to the problem of California carbon budgets because much of the air entering California is of oceanic origin and will

be depleted in ^{222}Rn. Application of this technique will require detailed analysis of ^{222}Rn source fields for California, because work has shown that ^{222}Rn emissions from soil can vary substantially with meteorology and soil moisture (Conen and Robertson 2002; Levin et al. 2002).

4.4.   Synthesis of Bottom-Up and Top-Down Methods

A crucial aspect of using atmospheric (or "top-down") methods to monitor California's CO_2 emissions will be to sensibly incorporate "bottom-up" information (e.g., ecosystem production from forest inventories and crop yields, fossil CO_2 emissions from improved inventory methods, eddy covariance CO_2 flux data from towers and aircraft flights, and ecosystem models of CO_2 exchange) in the inversion. This approach is an emerging area and developments in the NACP will be valuable to addressing these issues in California.

4.5.   Potential for Monitoring Non-CO$_2$ GHG Emissions

The approach that was applied here could also be profitably applied to quantify the atmospheric signals generated by surface emission of non-CO_2 GHGs. Because the relative uncertainties for fluxes of non-CO_2 GHGs are considerably larger than for CO_2 (Franco 2002), atmospheric budget (Biraud et al. 2002) and inverse approaches may be particularly effective in significantly reducing those uncertainties using atmospheric observations.

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6.0 Glossary

ABL	Atmospheric Boundary Layer
CARB	California Air Resources Board
CMAQ	Community Multiscale Air Quality Model
CO	Carbon Monoxide
CO_2	Carbon Dioxide
EPA	U.S. Environmental Protection Agency
GHG	Greenhouse Gas
IPCC	Intergovernmental Panel on Climate Change
LADCO	Lake Michigan Air Directors Consortium
NACP	North American Carbon Program
NCEP	National Center for Environmental Prediction
NEE	Net Ecosystem Exchange
NEI	EPA National Emissions Inventories
NOAA CMDL	U.S. National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory
OCO	NASA Orbiting Carbon Observatory
PIER	Public Interest Energy Research

Appendix A. Diurnal and Seasonal Variations in NEE

Figure A1 shows the diurnal variation in NEE for each ecosystem type in June. Black points indicate the average from all pixels in each day while the red bar indicates the mean (length indicating and standard error of the mean) over the 12 days included in the average. With the exception of (dryland) shrub, the ecosystems take up significant amounts of carbon during the day because temperatures are reasonably warm and water is not seriously limiting and release carbon back the atmosphere at night. The seasonal variation in NEE for the four months included in the simulations are shown in Figure A2. Forest, woody savanna, grassland, and shrub ecosystems show seasonal patterns of NEE a combination of sunlight, temperature and moisture responses but are considered to be near carbon balance on an annual basis. Agriculture is modeled as a significant net sink of carbon reflecting the active removal of biomass. Irrigated agriculture is considered uniformly well watered and hence does not experience any water limitation.
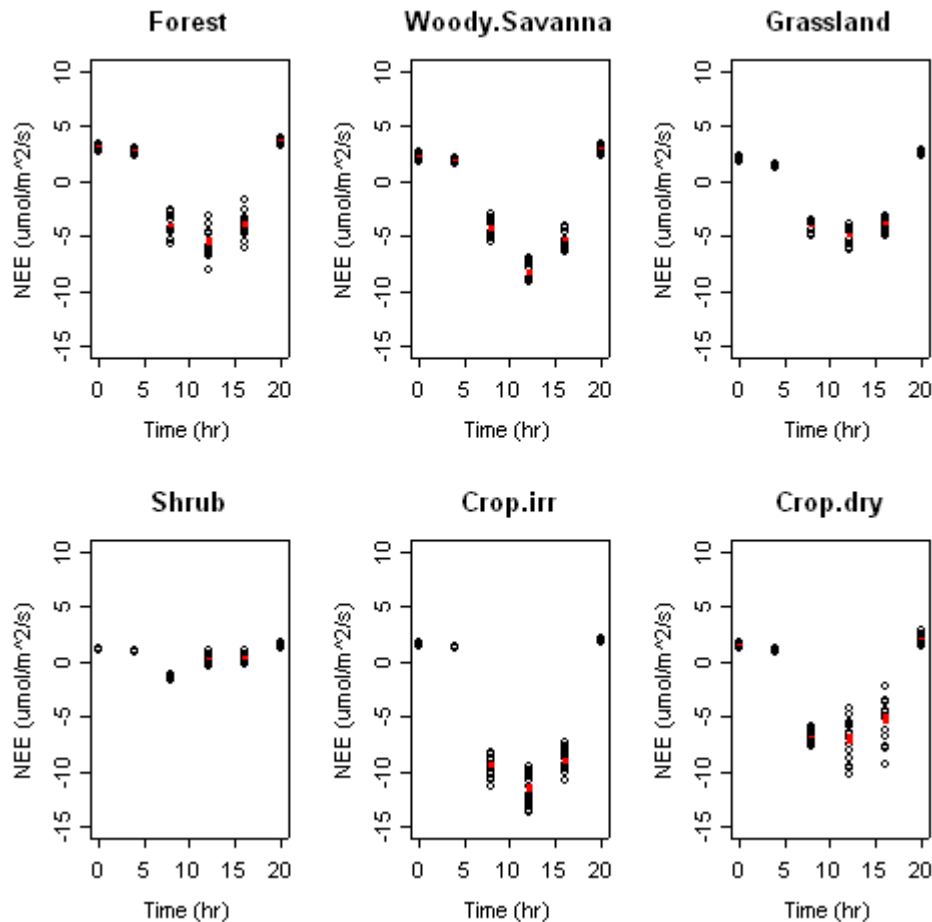
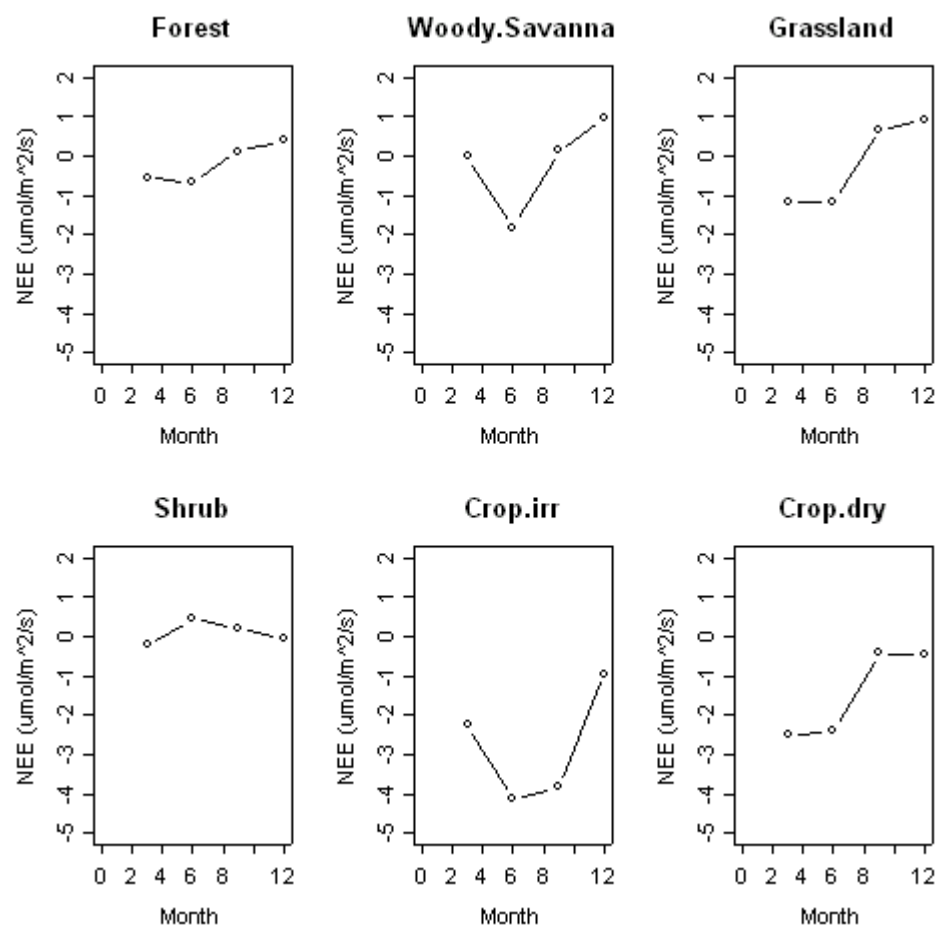**Figure A1. Diurnal variation in June NEE**

Figure A2. Seasonal variation in daily mean NEE

Appendix B. Seasonal Cycle of Mean Midday CO₂ Concentration Signals

These figures show the mean midday surface CO_2 concentration signals from NEE inside California (B1), NEE outside California (B2), fossil fuel CO_2 inside California (B3), and fossil fuel CO_2 outside California (B4). Signals are deviations from the CO_2 background from outside the modeling domain. CO_2 signals from NEE show strong seasonality signals due to ecosystem exchange, while signals from fossil fuel CO_2 show the direction of the mean wind (e.g., predominantly from the north in March), and the amount of mixing relative to average flow. In general, signals from NEE inside California are large enough to be measured with standard instrumentation at many terrestrial locations.
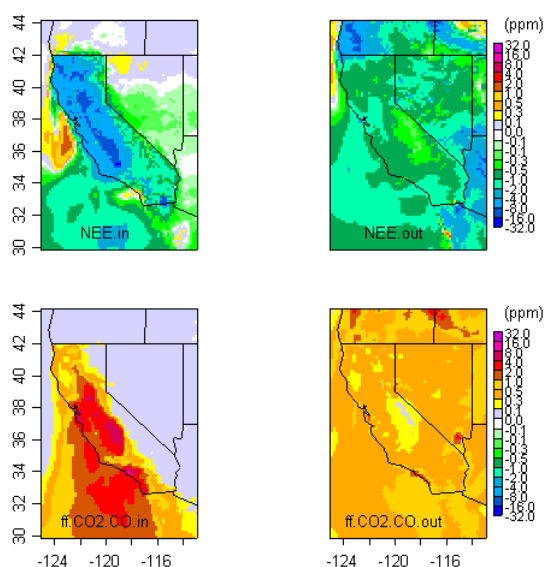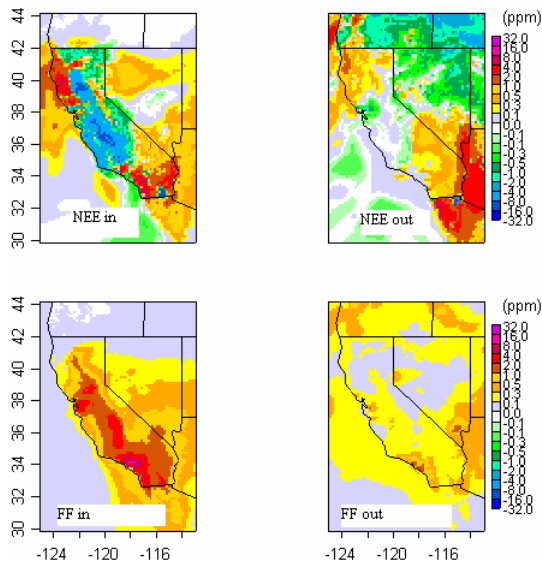

Figure B1. Signals in March
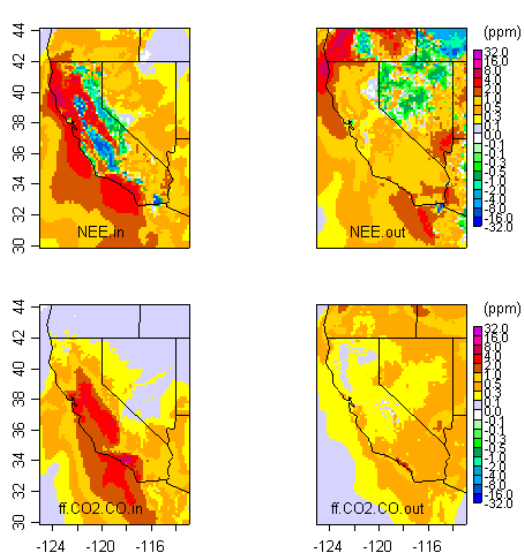

Figure B2. Signals in June (as in Figure 6)
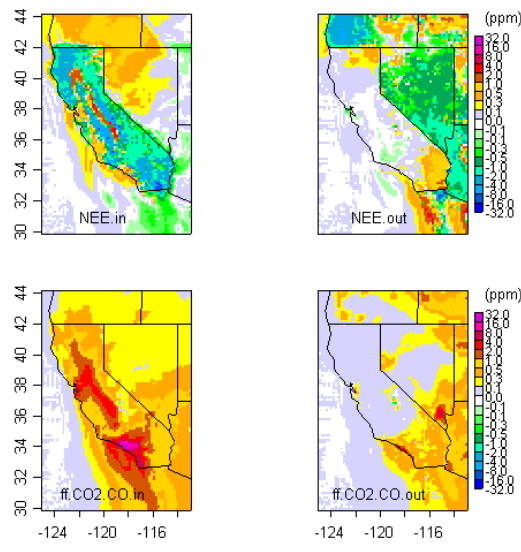

Figure B3. Signals in September

Figure B4. Signals in December

Appendix C. Seasonal Cycles of Mean Midday Concentration Signals at Observing Stations

The seasonal cycle of mean midday concentration CO_2 signal for each source and observing station are shown in Figure C1. For each observing station, the seasonal cycle in CO_2 signal is shown by lines connecting symbols with a common station number. Seasons are ordered March, June, September, December. The standard error of each mean midday value is shown as a thick vertical line. Signals from NEE.in show large seasonal variations because NEE varies with ecology, climate, and atmospheric transport. Signals from fossil fuel combustion show smaller seasonal variations that are caused largely by variations in atmospheric transport.
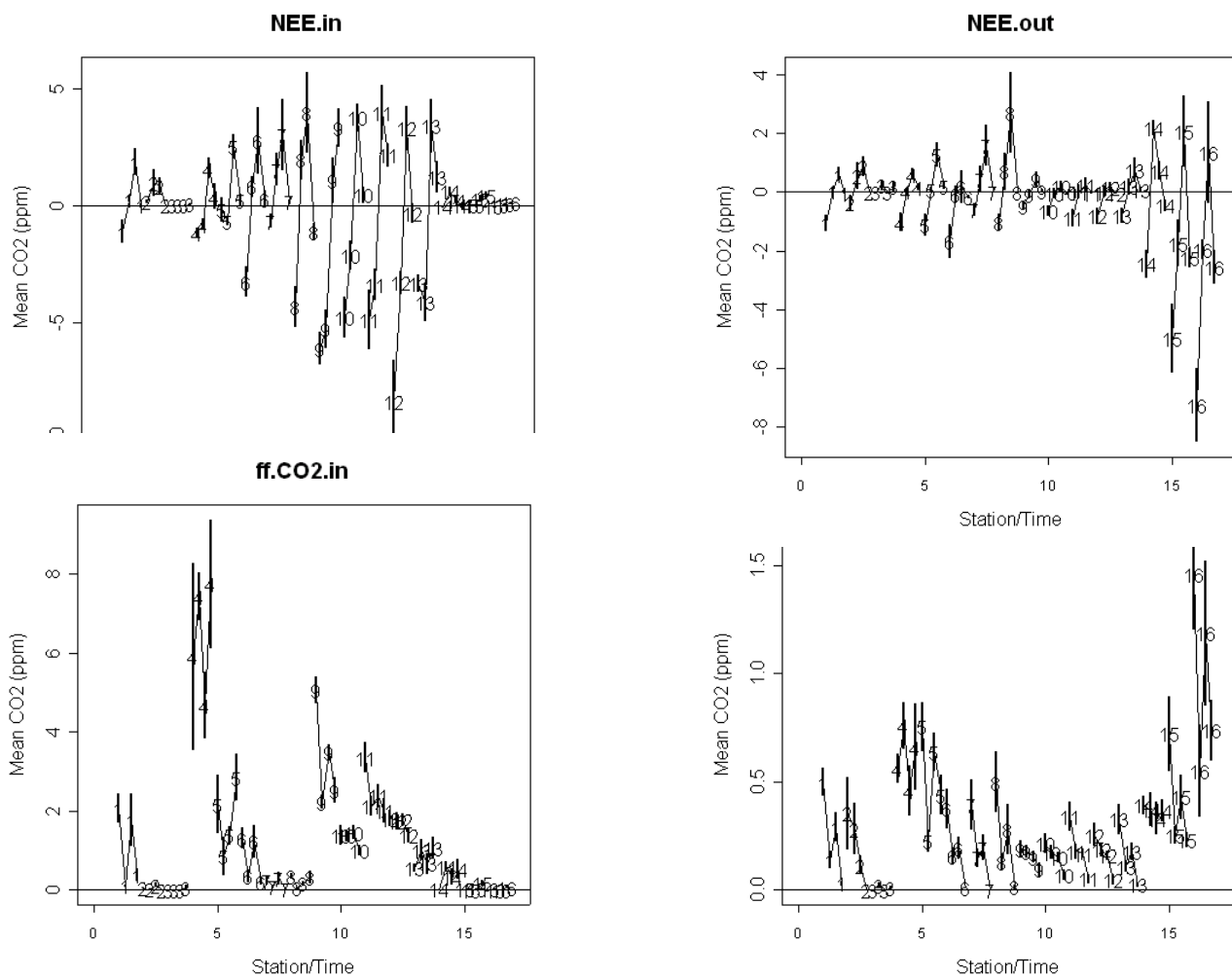

Figure C1. Seasonal cycles of mean midday concentration CO_2 signal for observing stations